

# **OPTION A: ANALYTICAL CHEM**

## **A9 — HL FURTHER NMR**

IB Chemistry  
TAD08



## A9 – HL – Further NMR

- A.9.1 Explain the use of tetramethylsilane (TMS) as the reference standard.  
(3)
- A.9.2 Analyze  $^1\text{H}$  NMR spectra. (3)
  - *Students should be able to interpret the following from  $^1\text{H}$  NMR spectra: number of peaks, area under each peak, chemical shift and splitting patterns. Treatment of spin–spin coupling constants will not be assessed, but students should be familiar with singlets, doublets, triplets and quartets.*



# Use of TMS

## A.9.1 Explain the use of tetramethylsilane (TMS) as the reference standard. (3)

- NMR peaks are measured in reference to a standard, in this case TMS (Tetramethylsilane –  $(\text{CH}_3)_4\text{Si}$ ).
  - TMS has 12 hydrogens – all in an identical environment and produces a sharp single peak that does not interfere with most organic molecules
  - Small amounts of TMS are added to each sample prior to NMR spectroscopy
    - TMS is
      - Unreactive
      - Non-toxic
      - Can be easily removed following analysis by simple evaporation.

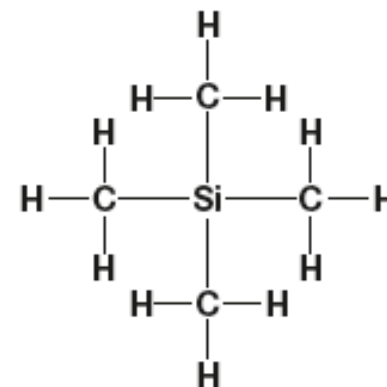


Figure 21.132 Structure of tetramethylsilane (TMS)



# NMR Multiplicity

## A.9.2 Analyze $^1\text{H}$ NMR spectra. (3)

- High resolution NMR gives rise to the **splitting pattern** of hydrogen peaks
  - The spin-spin splitting pattern (coupling) is a result of the adjacent (neighboring) carbon atoms' hydrogen atoms interfering with the signal. This can be used to our advantage
  - The  $n+1$  rule can be followed in which:
    - $n$  = the number of hydrogen atoms attached to the adjacent carbon
    - $+1$  = the hydrogen itself

# H on Adjacent C	# lines (multiplicity)	Relative intensities
1	2	1:1
2	3	1:2:1
3	4	1:3:3:1
4	5	1:4:6:4:1



# Multiplicity

Adjacent H's	Pascals Triangle	Multiplicity
n=0	1	Singlet
n=1	1 1	Doublet
n=3	1 2 1	Triplet
n=4	1 3 3 1	Quartet
n=5	1 4 6 4 1	Quintet

Splitting patterns  
for H<sub>a</sub>



Splitting patterns  
for H<sub>b</sub>

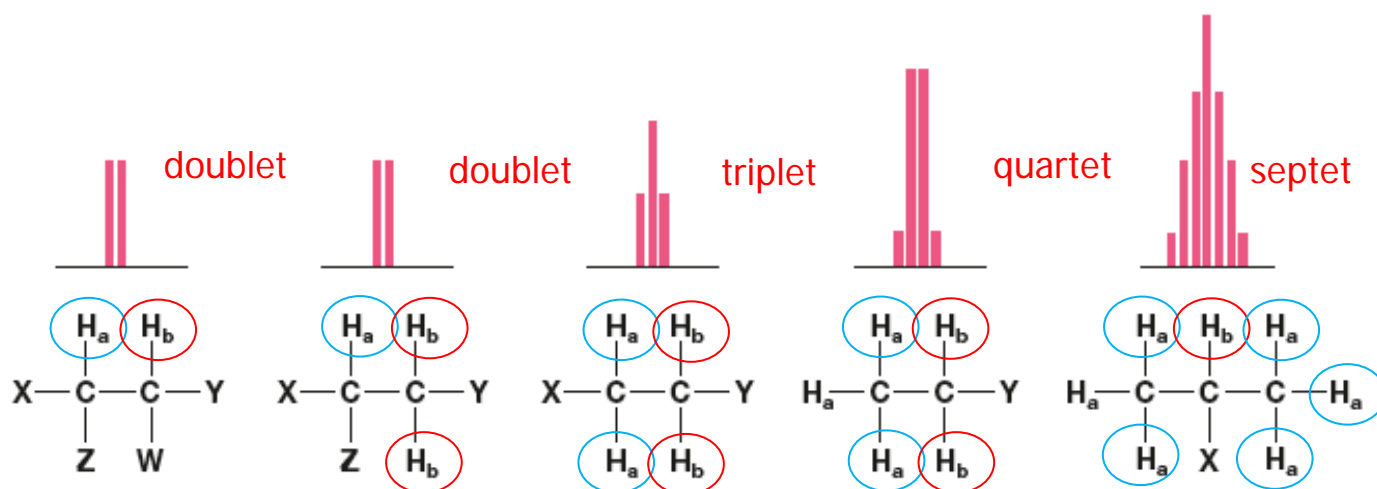
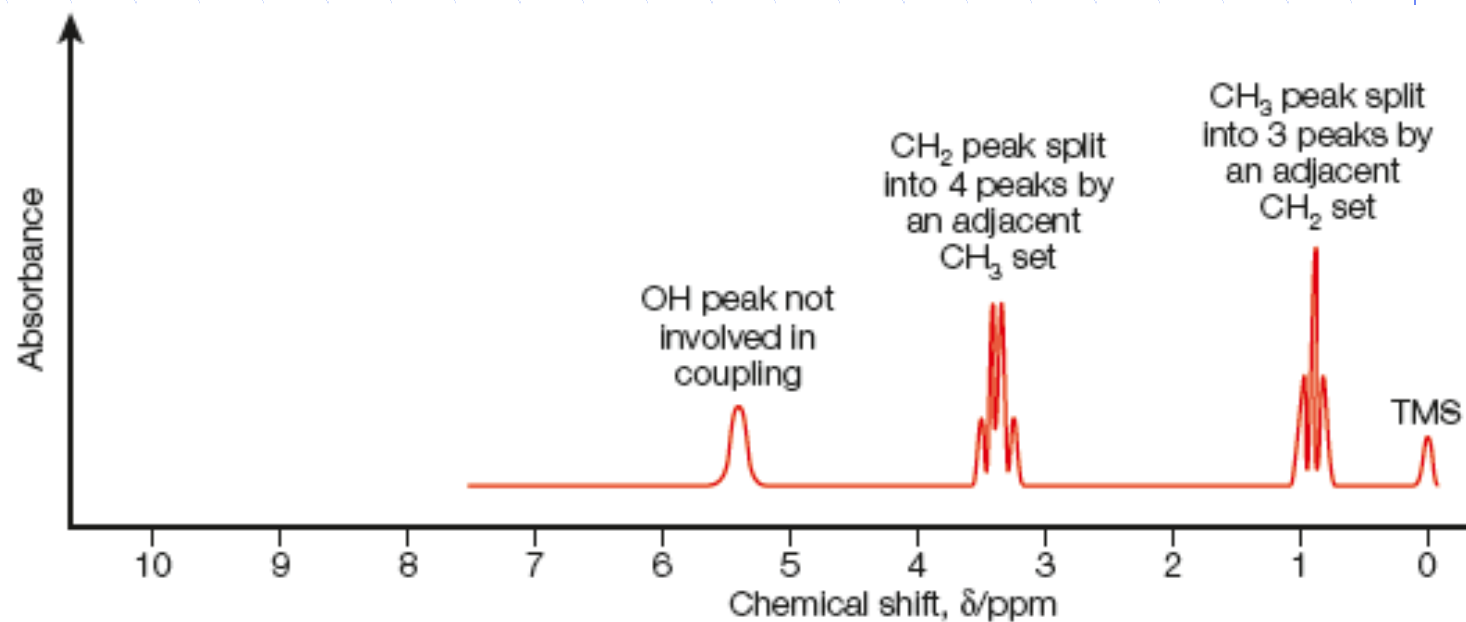


Figure 21.133 Commonly observed splitting patterns

# $^1\text{H}$ NMR High Res: Ethanol



**Figure 21.135** High resolution NMR spectrum of ethanol,  $\text{CH}_3\text{--CH}_2\text{--OH}$



# Multiple Techniques

- To determine the structural formula of "Compound X" you have studied the following:
  - Elemental Analyzer
    - Determines elements present and their percentages
    - Material undergoes complete combustion and gaseous products are analyzed by a Gas Chromatography system
  - Mass Spectrometry
    - Determines total mass and fractions may identify structure
    - Vaporized, Ionized, Accelerated, Deflected, Detected
  - IR Spectroscopy
    - Determines functional groups present
    - Radiated with low energy IR waves which vibrate and rotate IR active molecules
  - $^1\text{H}$  High Res NMR
    - Determines structure and organization of known composition
    - Radiated with low energy radio waves in the presence of a strong magnet



# Compound X – Elemental Analyzer

- The combustion of 100.0 g of compound  $C_xH_yO_z$  produced 244.31g carbon dioxide and 99.01g water:
  - $C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O$  (balancing is not needed)
    - $244.31g\ CO_2 \times \frac{12.01\ g\ C}{44.01\ g\ CO_2} = 66.67\ g\ C$
    - $99.01g\ H_2O \times \frac{2.02\ g\ H}{18.02\ g\ H_2O} = 11.11\ g\ H$
  - If all of the C and H in  $C_xH_yO_z$  is converted into  $CO_2$  and  $H_2O$  respectively, and we now know we know the total mass of  $C_xH_yO_z$ , we can then find the mass of O
    - $100.0\ g\ C_xH_yO_z - 66.67\ g\ C - 11.11\ g\ H = 22.22\ g\ O$
  - Convert each into moles
    - $66.67\ g\ C \times \frac{1\ mol\ C}{12.\ g\ C} = 5.56\ mol\ C$
    - $11.11\ g\ H \times \frac{1\ mol\ H}{1.\ g\ H} = 11.00\ mol\ H$
    - $22.22\ g\ O \times \frac{1\ mol\ O}{16.\ g\ O} = 1.39\ mol\ O$
- Find empirical formula
  - $C_{5.56}H_{11.11}O_{1.39} / 1.39 = C_4H_8O$





# Compound X – Mass Spec

- Ion at 72
  - This is the total mass of the compound
  - Empirical from Elemental Analyzer  $C_4H_8O = 72.12$
  - The Empirical formula is then the molecular formula
- Ion at 43
  - $CH_3CO^+$  (possible ketone)
- Ion at 29
  - $CH_3CH_2^+$  (possible backbone) or  $CHO^+$  (aldehyde – NOT Possible)

**Previous:**  
EA:  $C_4H_8O$

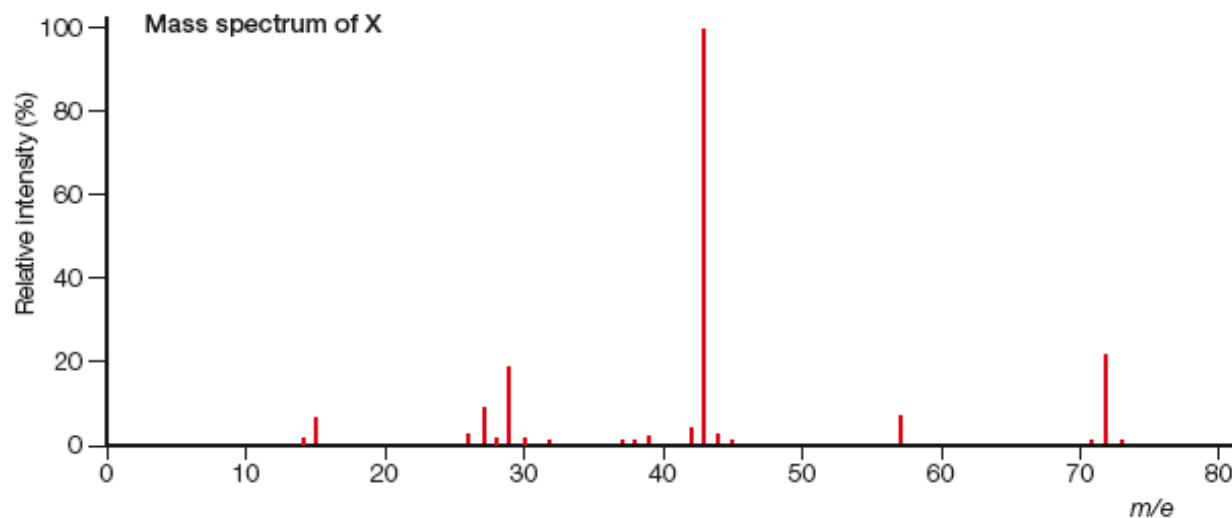


Figure 21.138 a The mass spectrum of compound X



# Compound X - IR

- Band at  $1718\text{ cm}^{-1}$ 
  - Carbonyl from
    - aldehyde (not possible)
    - Ketone (possible)
- Band at  $2900\text{ cm}^{-1}$ 
  - Presence of several C-H bonds

**Previous:**EA:  $\text{C}_4\text{H}_8\text{O}$ MS:  $\text{C}_4\text{H}_8\text{O}$ 

- Ketone
- $\text{CH}_3\text{CH}_2$

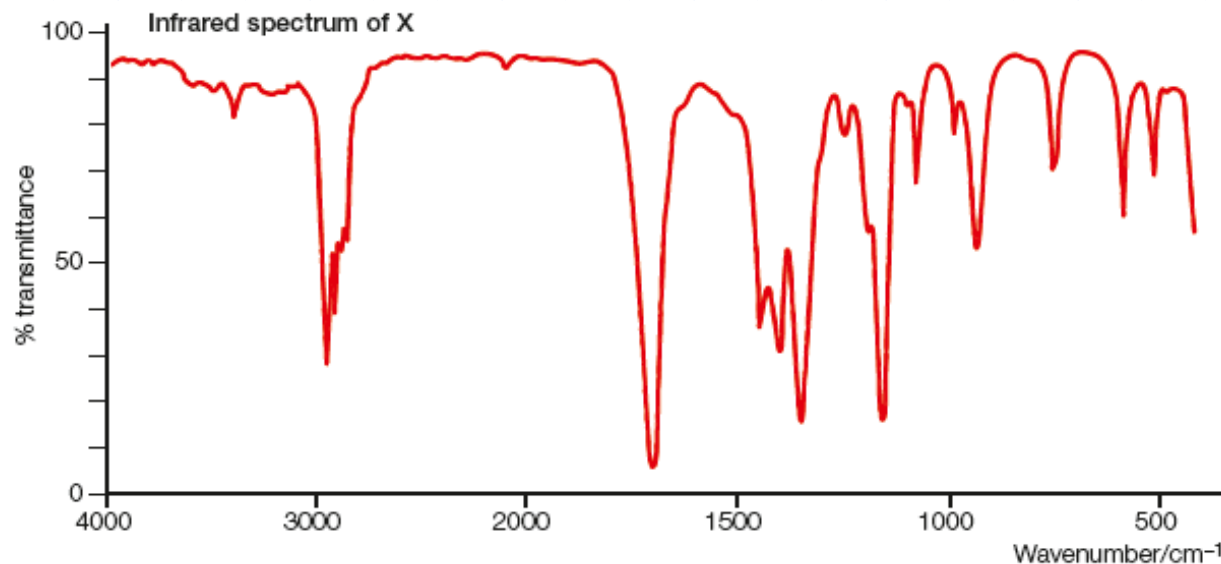
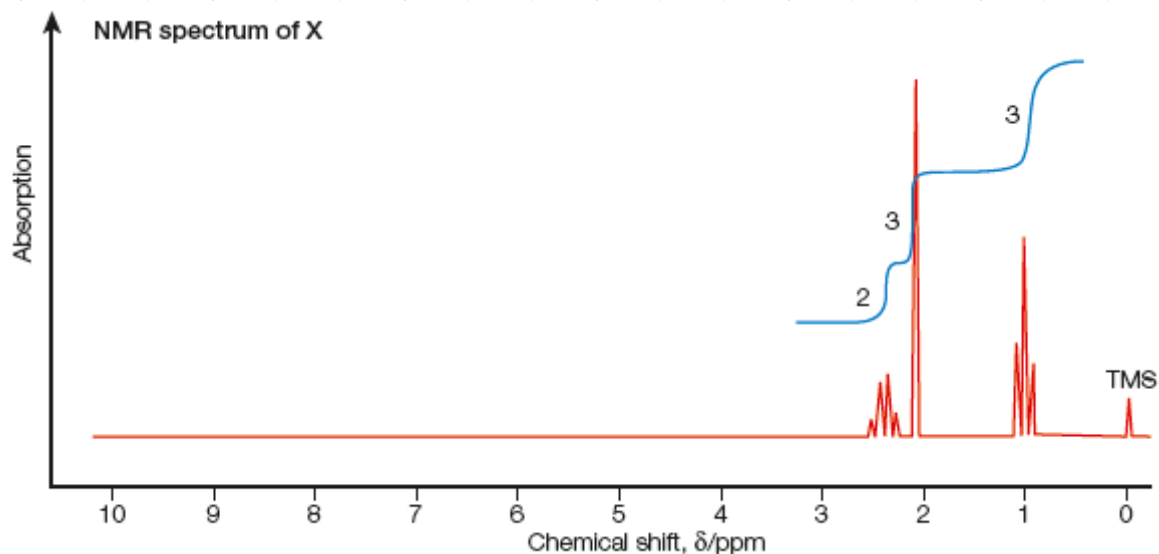
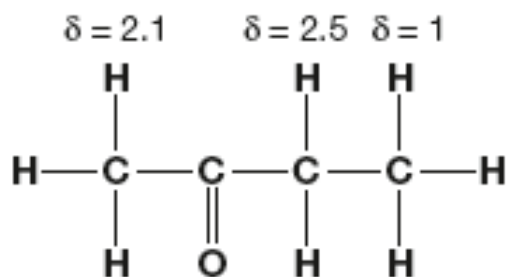


Figure 21.138 b The IR spectrum of compound X



- 0 = TMS
- Triplet (w/ x3 intensity) @ 1.0
- Singlet (w/ x3 intensity) @ 2.1
- Quartet (w/ x2 intensity) @ 2.5

IR: ketone + C-H



**Figure 21.138 c** The NMR spectrum of compound X



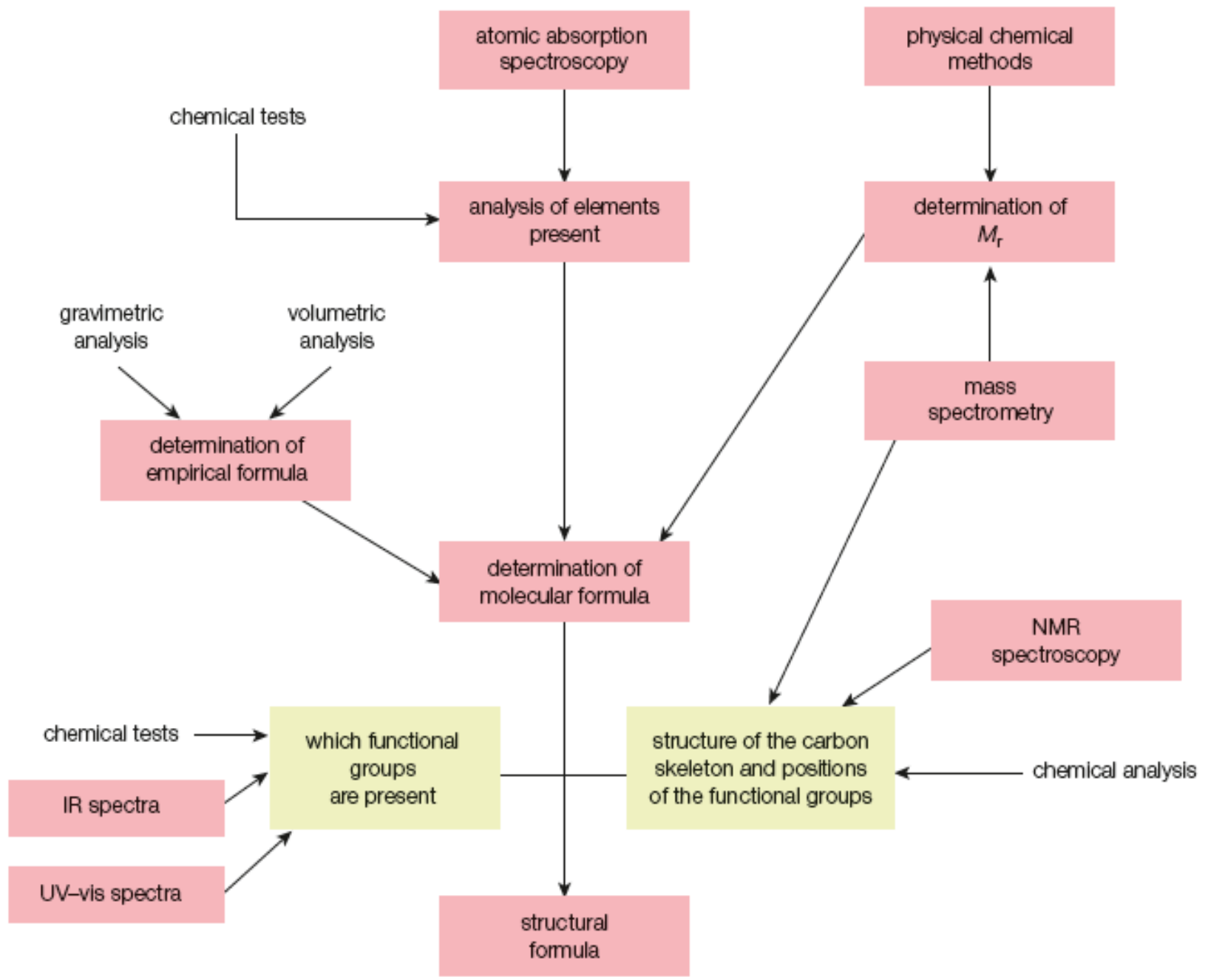


Figure 21.140 Summary of methods used to determine the structure of an organic compound